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MULTICOMPONENT SYSTEM FOR USE WITH DETERGENT SUBSTANCES

The present invention relates to a novel multicomponent system for use with detergent

INS A>

substances.

INS A> Particularly in the low-temperature range, conventional bleaching systems in household detergents are unsatisfactory. Below a washing temperature of 60°C, the standard bleaching agent H₂O₂/sodium perborate/sodium percarbonate must be activated by adding such chemical bleach activators as TAED (Tetraacetyl ethylenediamine) and SNOBS (Sodium p-isobutylbenzenesulfonate). Moreover, there is a demand for biocompatible bleaching systems with better 10 biodegradability and that can be used in lower doses for low-temperature clothes washing. While for protein starch and fat dissolution and for fiber treatment in the laundry process enzymes are already in use on an industrial scale, no enzymatic principle has thus far been available for detergent bleaches.

In International Patent Disclosure WO 91/05839, the use of various oxidative enzymes (oxidases and peroxidases) have been described for preventing "dye transfer". Peroxidases are known to be capable of bleaching various pigments (3-hydroxyflavon and betaine by horseradish 15 peroxidase, and carotene by peroxidase).

The aforementioned patent application describes the decoloration (or bleaching) of textile dyes that have been dissolved out of the laundry and are present in the washwater (conversion of a 20 dyed substrate into an undyed, oxidized substance). The enzyme is intended to have the advantage over hypochlorite, for example, which also attacks the dye or the fabric, of bleaching only dye that is present in dissolved form; hydrogen peroxide or a corresponding precursor, or hydrogen peroxide generated in situ, are involved in the catalysis of the decoloration. The enzyme reaction can be reinforced in part by adding additional oxidizable enzyme substrate, such as metal ions like Mn⁺⁺,

halogen ions such as Cl^- or Br^- , or organic phenols, such as p-hydroxy cinnamic acid and 2,4-dichlorophenol. Here it is postulated that short-lived radicals or other oxidized states of the added substrate are responsible for the bleaching or other modification of the dyed substance.

US Patent 4,776,768 describes the use of iron porphin, haemin chloride, or iron 5 phthalocyanine, or derivatives, together with hydrogen peroxide to prevent dye transfer. However, these substances are rapidly destroyed if there is an excess of peroxide, and the formation of hydrogen peroxide must therefore proceed in controlled fashion.

From International Patent Disclosures WO 94/12619, WO 94/12620 and WO 94/12621, methods are known in which the activity of the peroxidase is enhanced by so called enhancer 10 substances. Such enhancer substances are characterized in terms of their half-life in WO 94/12620. According to WO 94/12621, enhancer substances are characterized by the formula $A=N-N=B$, where A and B are each defined cyclical radicals. According to WO 94/12620, enhancer substances are organic chemicals that contain at least two aromatic rings, at least one of which is substituted with 15 respectively defined radicals.

All three applications pertain to dye transfer inhibition and to the use of the various enhancer substances along with peroxidases as a detergent additive or detergent composition in the laundry detergent field. The combination of these enhancer substances is restricted to peroxidases.

From International Patent Disclosure WO 92/18687, the use of mixtures containing 20 peroxidases is also known. A special system comprising oxidases and substrates suitable for them as well as hydrogen peroxide is described in German Published, Non-Examined Patent Application DE-OS 42 31 761. German Published, Non-Examined Patent Application DE-OS 19 18 729 relates to a further special detergent system, which comprises glucose and glucose oxidase (GOD), or starch, amyloglucosidase and glucose oxidase (GOD) as well as an additive comprising hydroxylamine or

hydroxylamine compounds, in which the hydroxylamine or its derivatives serve to inhibit the catalase that often occurs in GOD.

International Patent Disclosure PCT/EP 94/01967, finally, contains a multicomponent bleaching system for use with detergent substances comprising oxidation catalysts and oxidation agents as well as aliphatic, cycloaliphatic, heterocyclic or aromatic NO-, NOH- or H-NR-OH-containing compounds.

A disadvantage of all the previously known detergent systems is that the cleaning and bleaching action is still unsatisfactory, or that the mediator substances, as in PCT/EP 94/01087, must be added in excessive amounts, possibly leading to environmental and economic problems.

a **INS A3** **General Description of the Invention**

The object of the present invention is accordingly to furnish an improved multicomponent system for use with detergents that does not have the above disadvantages of the prior art and that instead increases the action of the actual mediator substances or regenerates *in situ*, that is, during the washing process.

This object is attained by a multicomponent system, containing

- a) optionally, at least one oxidation catalyst;
- b) at least one suitable oxidizing agent;
- c) at least one mediator, selected from the group comprising hydroxylamines, hydroxylamine derivatives, hydroxamic acids, hydroxamic acid derivatives, and the aliphatic, cycloaliphatic, heterocyclic or aromatic compounds that contain at least one N-hydroxy, oxime, N-oxy, or N,N'-dioxy function;
- d) at least one comediator, selected from the group comprising aryl-substituted alcohols, carbonyl compounds, aliphatic ethers, phenol ethers, and/or olefins (alkenes); and

e) optionally, a small quantity of at least one free amine of a respective mediator used.

It is surprising that when the aforementioned comediators are added to the aforementioned mediators, optionally together with the free amines of the respective mediators and oxidation catalysts, on the one hand the bleaching action of detergents can be improved considerably, and on 5 the other the consumption of mediators can be reduced.

According to the invention, either one or more of the aforementioned mediators and co-mediators can be used. It is preferable to use one mediator and one comediator. It is also conceivable to use one mediator and two or more comediators. Conversely, it is also possible to use two or more mediators with one comediator.

10 The substances in the multicomponent bleaching system listed in paragraphs a), b), c), d), and e) are preferably used in a ratio of 2:0.2:10:0.2:0.2, and each component in the system can be multiplied by from 2 to 10.

The individual components of the multicomponent system according to the invention will be described in further detail below:

15 Oxidation Catalysts

The multicomponent system of the invention preferably contains at least one oxidation catalyst. Enzymes are preferably used as the oxidation catalysts. The term "enzyme" also includes enzymatically active proteins or peptides or prosthetic groups of enzymes.

As the enzyme, in the multicomponent system of the invention, oxidoreductases of classes 20 1.1.1 through 1.97 according to the International Enzyme Nomenclature, Committee of the International Union of Biochemistry and Molecular Biology (Enzyme Nomenclature, Academic Press, Inc., 1992, pp. 24-154), can be used.

Preferably, enzymes of the following named classes are used:

Enzymes of class 1.1, which include all the dehydrogenases that act on primary and secondary alcohols and semiacetals, and which as acceptors have NAD⁺ or NADP⁺ (subclass 1.1.1.), cytochromes (1.1.2), oxygen (O₂) (1.1.3), disulfides (1.1.4), quinones (1.1.5), or other acceptors (1.1.99). From this class, the enzymes of class 1.1.5 with quinones as acceptors and the enzymes of 5 class 1.1.3. with oxygen as an acceptor are especially preferred and in this latter class cellobiose: quinone-1-oxidoreductase (1.1.5.1) is particularly preferred.

Enzymes of class 1.2 can also be used. This enzyme class (1.1.5.1) includes enzymes of the type that oxidize aldehydes to form the corresponding acids or oxo groups. The acceptors may be NAD⁺, NADP⁺ (1.2.1.), cytochromes (1.2.2), oxygen (1.2.3), sulfides (1.2.4), iron-sulfur proteins 10 (1.2.5), or other acceptors (1.2.99). Here, the enzymes of group (1.2.3) with oxygen as the acceptor are especially preferred.

Enzymes of class 1.3 can also be used. This class summarizes enzymes that act on CH-CH groups of the donor. The corresponding acceptors are NAD⁺, NADP⁺ (1.3.1), cytochromes (1.3.2), oxygen (1.3.3), quinones or related compounds (1.3.5), iron-sulfur proteins (1.3.7), or other acceptors (1.3.99). Once again, the enzymes of class (1.3.3) with oxygen as an acceptor and (1.3.5) with quinones etc. as an acceptor are especially preferred. 15

The enzymes of class 1.4 that act on CH-NH₂ groups of the donor can also be used. The corresponding acceptors are NAD⁺, NADP⁺ (1.4.1.), cytochromes (1.4.2), oxygen (1.4.3), disulfides (1.4.4), iron-sulfur proteins (1.4.7), or other acceptors (1.4.99) Once again, enzymes of class 1.4.3 20 with oxygen as an acceptor are especially preferred.

Also usable are enzymes of class 1.5 that act on CH-NH groups of the donor. The corresponding acceptors are NAD⁺, NADP⁺ (1.5.1), oxygen (1.4.3), disulfides (1.5.4), quinones

(1.5.5), or other acceptors (1.5.99). Once again, enzymes with oxygen (O_2) (1.5.3) and with quinones (1.5.5) as acceptors are especially preferred.

Enzymes of class 1.6 that act on NADH or NADPH can also be used. In this case the acceptors are $NADP^+$ (1.6.1), heme proteins (1.6.2), disulfides (1.6.4), quinones (1.6.5), NO_2 groups 5 (1.6.6), and a flavin (1.6.8) or some other acceptors (1.6.99). Enzymes of class 1.6.5 with quinones as the acceptors are especially preferred here.

Furthermore, enzymes of class 1.7 that act on other NO_2 compounds as donors and that as acceptors have cytochromes (1.7.2), oxygen (O_2) (1.7.3), iron-sulfur proteins (1.7.7) or others (1.7.99) can also be used. Here, class 1.7.3 with oxygen as the acceptor is especially preferred.

10 Enzymes of class 1.8 that act on sulfur groups as donors and that as acceptors have NAD^+ , $NADP^+$ (1.8.1) cytochromes (1.8.2), oxygen (O_2) (1.8.3), disulfides (1.8.4), quinones (1.8.5), iron-sulfur proteins (1.8.7), or others (1.8.99) can also be used. Class 1.8.3 with oxygen (O_2) and (1.8.5) with quinones as acceptors is especially preferred.

15 Also usable are enzymes of class 1.9, which act on heme groups as donors and which have as acceptors oxygen (O_2) (1.9.3), NO_2 compounds (1.9.6) and others (1.9.99). Here, group 1.9.3 with oxygen (O_2) as an acceptor (cytochromooxidases) is especially preferred here.

Moreover, enzymes of class 1.12 that act on hydrogen as a donor can be considered. The acceptors are NAD^+ or $NADP^+$ (1.12.1) or others (1.12.99).

The enzymes that can be used also include those of classes 1.13 and 1.14 (oxygenases).

20 Enzymes of class 1.15, which act on superoxide radicals as acceptors, can also be named. Here, the superoxide dismutase (1.15.1.1) is especially preferred.

In addition, enzymes of class 1.16 can be used. NAD^+ or $NADP^+$ (1.16.1) or oxygen (O_2) (1.16.3) act as acceptors. Especially preferred here are enzymes of class 1.16.3.1

(ferroxidases, such as ceruloplasmin). Others that can be named are those enzymes that belong to group 1.17 (action on CH₂ groups which are oxidized to form -CHOH-), 1.18 (action on reduced ferredoxin as a donor), 1.19 (action on reduced flavodoxin as a donor), and 1.97 (other oxidoreductases).

5 Among the enzymes that are very particularly preferred are those in class 1.10 that act on biphenols and related compounds. They catalyze the oxidation of biphenols and ascorbates. Functioning as acceptors are NAD⁺, NADP⁺ (1.10.1), cytochromes (1.10.2), oxygen (1.10.3), or others (1.10.99). Of these, again, enzymes of class 1.10.3 with oxygen (O₂) as the acceptor are especially preferred.

10 Of the enzymes of this class, the enzymes catechol oxidase (tyrosinase) (1.10.3.1), L-ascorbate oxidase (1.10.3.3), O-aminophenol oxidase (1.10.3.4) and laccase (benzenediol: oxygen oxidoreductase) (1.10.3.2); the laccases (benzenediol: oxygen oxidoreductase) (1.10.3.2) are especially preferred.

15 Also particularly preferred are the enzymes of group 1.11 that act on a peroxide as the acceptor. This single subclass (1.11.1) contains the peroxidases.

Also especially preferred are the enzymes of group 1.11., which act on a peroxide as an acceptor.

20 This single subclass (1.11.1) includes the peroxidases. Very particularly preferred here are the cytochrome C peroxidases (1.11.1.5), catalase (1.11.1.6), peroxidase (1.11.1.7), iodide peroxidase (1.11.1.8), glutathione peroxidase (1.11.1.9), chloride peroxidase (1.11.1.10), L-ascorbate peroxidase (1.11.1.11), phospholipid hydroperoxide glutathione peroxidase (1.11.1.12), manganese peroxidase (1.12.1.13), diarylpropane peroxidase (ligninase, lignin peroxidase).

These enzymes are commercially available or can be prepared by standard methods.

Organisms that can be considered for producing the enzymes are for instance plants, animal cells, bacteria, and fungi. In principle, both naturally occurring organisms and organisms altered by gene technology can be enzyme producers. Parts of singlecell or multicell organisms, and above all cell cultures, are also conceivable as enzyme producers.

Particular for producing the preferred enzymes of group 1.11.1, but above all from group 1.10.3, and especially for producing the laccases, white rotting fungi such as Pleurotus, Phlebia and Trametes, for instance, are used.

Oxidation Agent

The multicomponent system of the invention includes at least one oxidation agent. As the oxidizing agent, air, oxygen, ozone, H_2O_2 , organic peroxides, peracids such as peracetic acid, performic acid, persulfuric acid, permanganic acid, metachloroperoxybenzoic acid, perchloric acid, perborates, peracetates, persulfates, peroxides, or oxygen species and their free radicals thereof, such as OH, OOH and superoxide (O_2^-) and singlet oxygen, ozonide, dioxygenyl cation (O_2^+), dioxiranes, dioxitanes, or Fremy radicals can for instance be used.

The oxidation agents used are preferably those that can either be generated by the corresponding oxidoreductases, such as dioxiranes from laccases plus carbonyls, or that can chemically regenerate the mediator (for instance, Caro's acid + benzotriazole produces hydroxybenzotriazole) or that can convert these directly.

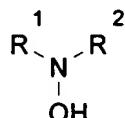
Mediators

The multicomponent system according to the invention contains as a mediator (component c) preferably at least one compound that contains an N-hydroxy, oxime, N-oxy or D-dioxy function and/or one of the compounds named below of formulas I, II, III, IV or V; the compounds of

formulas II, III, IV and V are preferred, the compounds of formulas II, IV and V are especially preferred, and compounds of formulas IV and V are very particularly preferred.

Hydroxylamines can for instance be used according to the invention (open-chained or cyclical, aliphatic or aromatic, heterocyclical), of the general formula

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in which the substituents R¹ and R², which may be the same or different, independently of one another represent one of the following groups: hydrogen, C₁-C₁₂ alkyl, carbonyl C₁-C₆ alkyl, phenyl, aryl, of which C₁-C₁₂ alkyl, carbonyl C₁-C₆ alkyl, phenyl, aryl groups may be unsubstituted or may also be substituted once or multiple times with the radical R³.

The radical R³ may represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxy and salts and esters thereof; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, sulfonyl, their esters and salts, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and their salts and esters. The amino, carbamoyl and sulfamoyl groups of the radical R³ may be unsubstituted or may be substituted once or two times with hydroxy, C₁-C₃ alkyl, C₁-C₃ alkoxy.

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The radicals R¹ and R² can jointly form a group -B-. In that case, -B- represents one of the following groups: (-CHR4-)_n, (CR4=CH-)_m. n represents an integer from 1 to 6 and m represents an integer from 1 to 3.

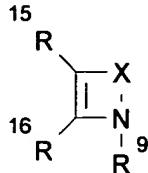
R⁴ is a substituent that is defined like R³.

Examples of hydroxylamines that can be used are: N,N- dipropylhydroxylamine, N,N-diisopropylhydroxylamine, N- hydroxypyrrolidine, N-hydroxypiperidine, N-

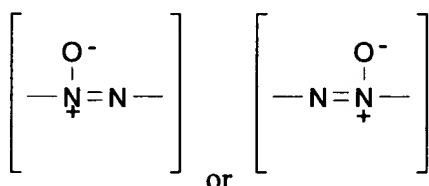
hydroxyhexahydroazepine, N,N-dibenzylhydroxylamine, phenylhydroxylamine, 3-hydroxylamino-3-phenyl propionic acid, 2-hydroxylamino-3-phenyl propionic acid, N- sulfomethylhydroxylamine, N-sulfomethylhydroxylamine.

Compounds of general formula II are:

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X stands for one of the following groups: (-N=N-), (-N=CR¹⁰-)_p, (-CR¹⁰=N-)_p, (-CR¹¹=CR¹²-)_p,



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H10 and p is equal to 1 or 2.

The radicals R⁹ to R¹², R¹⁵ and R¹⁶ may be the same or different and independently of one another can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, sulfonyl, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and 15 their salts and esters. The amino, carbamoyl and sulfamoyl groups of the radicals R⁹ to R¹², R¹⁵ and R¹⁶ may be unsubstituted or may also be substituted once or two times with hydroxyl, C₁-C₃ alkyl, C₁-C₃ alkoxy. The radicals R¹⁵ and R¹⁶ can form a common group -G-. -G- represents one of the following groups:

(-CR⁵=CR⁶-CR⁷=CR⁸-) or (-CR⁸=CR⁷-CR⁶=CR⁵-).

The radicals R⁵ to R⁸ may be the same or different and independently of one another can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl, C₁-C₆ alkyl, phenyl, sulfono, esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, 5 phosphonoxy and their salts and esters. The amino, carbamoyl and sulfamoyl groups of the radicals R⁵ to R⁸ may be unsubstituted or may also be substituted once or two times with hydroxy, C₁-C₃ alkyl, C₁-C₃ alkoxy.

The C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl and aryl groups of radicals R⁵ to R⁸ may be unsubstituted or may be substituted one or two times with the radical R¹⁸.

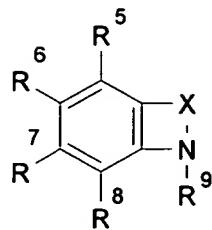
10 The radical R¹⁸ can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and their salts and esters, amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, aryl, and their esters and salts. The carbamoyl, sulfamoyl and amino groups of the radical R¹⁸ may be unsubstituted or may also be substituted once or two times with the radical R¹⁹.

15 The radical R¹⁹ may represent one of the following groups: hydrogen; hydroxyl, formyl, carboxyl and their salts and esters; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl and aryl.

Examples of the above-named compounds are

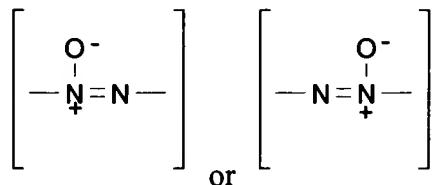
20 1-hydroxy-1,2,3-triazole-4,5-dicarboxylic acid, 1- phenyl-1H-1,2,3-triazole-3-oxide, 5-chloro-1-phenyl-1H-1,2,3- triazole-3-oxide, 5-methyl-1-phenyl-1H-1,2,3-triazole-3- oxide, 4-(2,2-dimethylpropanoyl)-1-hydroxy-1H-1,2,3-triazole, 4-hydroxy-2-phenyl-2H-1,2,3-triazole-1-oxide, 2,4,5- triphenyl-2H-1,2,3-triazole-1-oxide, 1-benzyl-1H-1,2,3- triazole-3-oxide, 1-benzyl-4-chloro-1H-1,2,3-triazole-3- oxide, 1-benzyl-4-bromo-1H-1,2,3-triazole-3-oxide, and 1- benzyl-4-methoxy-1H-1,2,3-triazole-3-oxide.

Compounds of the general structure III are:



X stands for one of the following groups: (-N=N-), (-N=CR¹⁰-)_p, (-CR¹⁰=N-)_p,

5 (-CR¹¹=CR¹²-)_p



and p is equal to 1 or 2.

The radicals R⁵ to R¹² may be the same or different and independently of one another can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof, amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, aryl, sulfono esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonoxy and their salts and esters. The amino, carbamoyl and sulfamoyl groups of the radicals R⁵ to R¹² may be unsubstituted or may also be substituted once or two times with hydroxyl, C₁-C₃ alkyl, C₁-C₃ alkoxy. The C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, aryl, aryl C₁-C₆ alkyl groups of radicals R⁵ to R¹² may be unsubstituted or substituted one or two times with the radical R¹³.

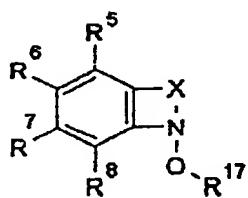
The radical R¹³ can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and their salts and esters; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, aryl, sulfono, sulfeno, sulfino, and their esters and salts. The carbamoyl, sulfamoyl,

amino groups of the radical K^{13} may be unsubstituted or may also be substituted once or two times with the radical R^{14} .

The radical R¹⁴ may represent one of the following groups: hydrogen; hydroxyl, formyl, carboxyl and their salts and esters; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl or aryl.

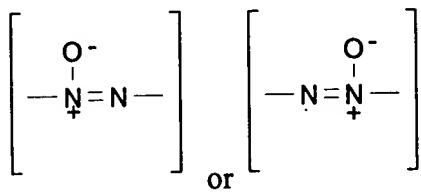
Examples are: 1-hydroxy-benzimidazoles, such as 1- hydroxy-benzimidazole-2-carboxylic acid, 1-hydroxy- benzimidazole, 2-methyl-1-hydroxy-benzimidazole, 2-phenyl-1- hydroxy-benzimidazole, and 1-hydroxyindoles, such as 2- phenyl-1-hydroxyindole.

Substances of general formula IV are:



X stands for one of the following groups: (-N=N-), (-N=CR¹⁰-)_m, (-CR¹⁰=N-)_m,

$$20 \quad (-CR^{11}=CR^{12}-)_m$$

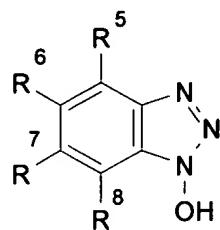


and m is equal to 1 or 2.

For the radicals R⁵ to R⁸ and R¹⁰ to R¹² what has been said above applies.

R¹⁷ can be hydrogen, C₁-C₁₀ alkyl, C₁-C₁₀ carbonyl, of which C₁-C₁₀ alkyl and C₁-C₁₀ carbonyl can be unsubstituted or mono- or polysubstituted with a radical R¹⁸, which is defined like R³.

5 Of the substances of Formula IV, in particular derivatives of 1-hydroxybenzotriazole and of the tautomeric benzotriazole-1-oxide, as well as their esters and salts, are preferred (compounds of formula V):



The radicals R⁵ to R⁸ may be the same or different and independently of one another can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and salts and esters thereof; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, sulfono esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and their salts and esters. The amino, carbamoyl and sulfamoyl groups of the radicals R⁵ to R⁸ may be unsubstituted or may also be substituted once or two times with hydroxyl, C₁-C₃ alkyl, C₁-C₃ alkoxy. The C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl or aryl groups of radicals R⁵ to R⁸ may be unsubstituted or may also be substituted one or mono- or polysubstituted with the radical R¹⁸.

The radical R¹⁸ can represent one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and their salts and esters; amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl, aryl, sulfono, sulfeno, sulfino, and their esters and salts. The carbamoyl, sulfamoyl, amino groups of the radical R¹⁸ may be unsubstituted or may also be substituted once or two times

with the radical R¹⁹. The radical R¹⁹ may represent one of the following groups: hydrogen; hydroxyl, formyl, carboxyl and their salts and esters, amino, nitro, C₁-C₁₂ alkyl, C₁-C₆ alkyloxy, carbonyl C₁-C₆ alkyl, phenyl or aryl.

Examples of the compounds named are 1-H- hydroxybenzotriazoles, such as: 1-

5 hydroxybenzotriazole, 1- hydroxybenzotriazole-6-sulfonic acid, 1-hydroxybenzotriazole- 6-carboxylic acid, 1-hydroxybenzotriazole-6-N- phenylcarboxamide, 5-ethoxy-6-nitro-1-hydroxybenzotriazole, 4-ethyl-7-methyl-6-nitro-1-hydroxybenzotriazole, 2,3-bis-(4- ethoxyphenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole, 2,3-bis-(2-bromo-4-methylphenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole, 2,3-bis-(4-bromophenyl)-4,6-dinitro- 2,3-dihydro-1-hydroxybenzotriazole, 2,3-bis-(4- carboxyphenyl)-4,6-dinitro-2,3-dihydro-1- hydroxybenzotriazole, 4,6-bis-(trifluoromethyl)-1- hydroxybenzotriazole, 5-bromo-1-hydroxybenzotriazole, 6- bromo-1-hydroxybenzotriazole, 4-bromo-7-methyl-1- hydroxybenzotriazole, 5-bromo-7-methyl-6-nitro-1-hydroxybenzotriazole, 4-bromo-6-nitro-1-hydroxybenzotriazole, 6-bromo-4-nitro-1-hydroxybenzotriazole, 4-chloro-1- hydroxybenzotriazole, 6-chloro-5-isopropyl-1-hydroxybenzotriazole, 5-chloro-6-methyl-1-hydroxybenzotriazole, 6-chloro-5-methyl-1-hydroxybenzotriazole, 4-chloro-7-methyl-6-nitro-1- hydroxybenzotriazole, 5-chloro-1-hydroxybenzotriazole, 6- chloro-1-hydroxybenzotriazole, 4-chloro-5-methyl-1-hydroxybenzotriazole, 5-chloro-4-methyl-1- hydroxybenzotriazole, 4-chloro-6-nitro-1-hydroxybenzotriazole, 7-chloro-1-hydroxybenzotriazole, 20 6- diacetylamino-1-hydroxybenzotriazole, 2,3-dibenzyl-4,6- dinitro-2,3-dihydro-1-hydroxybenzotriazole, 4,6-dibromo-1- hydroxybenzotriazole, 4,6-dichloro-1-hydroxybenzotriazole, 5,6-dichloro-1-hydroxybenzotriazole, 4,5-dichloro-1-hydroxybenzotriazole, 4,7-dichloro-1-hydroxybenzotriazole, 5,7-dichloro-6-nitro-1-hydroxybenzotriazole, 5,6-dimethoxy-1-

hydroxybenzotriazole, 2,3-di[2]naphthyl-4,6-dinitro-2,3- dihydro-1-hydroxybenzotriazole, 4,6-dinitro-1- hydroxybenzotriazole, 4,6-dinitro-2,3-diphenyl-2,3-dihydro-1- hydroxybenzotriazole, 4,6-dinitro-2,3-di-p-tolyl-2,3-dihydro- 1-hydroxybenzotriazole, 5-hydrazino-7-methyl-4-nitro-1-hydroxybenzotriazole, 5,6-dimethyl-1-hydroxybenzotriazole, 4- methyl-1-hydroxybenzotriazole, 5-

5 methyl-1- hydroxybenzotriazole, 6-methyl-1-hydroxybenzotriazole, 5-(1- methylethyl)-1-hydroxybenzotriazole, 4-methyl-6-nitro-1- hydroxybenzotriazole, 6-methyl-4-nitro-1-hydroxybenzotriazole, 5-methoxy-1-hydroxybenzotriazole, 6- methoxy-1-hydroxybenzotriazole, 7-methyl-6-nitro-1- hydroxybenzotriazole, 4-nitro-1-hydroxybenzotriazole, 6- nitro-1-hydroxybenzotriazole, 6-nitro-4-phenyl-1- hydroxybenzotriazole, 5-phenylmethyl-1-hydroxybenzotriazole, 4-trifluoromethyl-1-hydroxybenzotriazole, 5-trifluoromethyl- 1-hydroxybenzotriazole, 6-trifluoromethyl-1- hydroxybenzotriazole, 4,5,6,7-tetrachloro-1-hydroxybenzotriazole, 4,5,6,7-tetrafluoro-1- hydroxybenzotriazole, 6-tetrafluoroethyl-1-hydroxybenzotriazole, 4,5,6-trichloro-1-hydroxybenzotriazole, 4,6,7-trichloro-1-hydroxybenzotriazole, 6-sulfamido-1- hydroxybenzotriazole, 6-N,N-diethylsulfamido-1-hydroxybenzotriazole, 6-N-methylsulfamido-1- hydroxybenzotriazole, 6-(1H-1,2,4-triazole-1-ylmethyl)-1- hydroxybenzotriazole, 6-(5,6,7,8-tetrahydroimidazo-[1,5- a]pyridin-5-yl)-1-hydroxybenzotriazole, 6-(phenyl-1H-1,2,4- triazole-1-ylmethyl)-1-hydroxybenzotriazole, 6-[(5-methyl-1H- imidazole-1-yl)phenylmethyl]-1-hydroxybenzotriazole, 6-[(4-methyl-1H-imidazole-1-yl)phenylmethyl]-1- hydroxybenzotriazole, 6-[(2-methyl-1H-imidazole-1-yl)phenylmethyl]-1-hydroxybenzotriazole, 6-(1H-imidazole-1- yl)phenylmethyl]-1-hydroxybenzotriazole, 6-(1H-imidazole-1- ylphenylmethyl)-1-hydroxybenzotriazole, 6-[1(1H-imidazole-1- yl)ethyl]-1-hydroxybenzotriazole monohydrochloride.

In this connection, the following salts should also be mentioned:

1-hydroxybenzotriazole, sodium salt.

1-hydroxybenzotriazole, potassium salt.

1-hydroxybenzotriazole, lithium salt.

1-hydroxybenzotriazole, ammonium salt.

5 1-hydroxybenzotriazole, calcium salt.

1-hydroxybenzotriazole, magnesium salt.

1-hydroxybenzotriazole-6-sulfonic acid, monosodium salt.

Other examples of compounds of formulas IV and V that can be used according to the

invention are 3H-benzotriazole- 1-oxides, such as: 3H-benzotriazole-1-oxide, 6-acetyl-3H-

10 benzotriazole-1-oxide, 5-ethoxy-6-nitro-3H-benzotriazole-1- oxide, 4-ethyl-7-methyl-6-nitro-3H-
benzotriazole-1-oxide, 6- amino-3,5-dimethyl-3H-benzotriazole-1-oxide, 6-amino-3- methyl-3H-
benzotriazole-1-oxide, 5-bromo-3H-benzotriazole-1- oxide, 6-bromo-3H-benzotriazole-1-oxide, 4-
bromo-7-methyl-3H- benzotriazole-1-oxide, 5-bromo-4-chloro-6-nitro-3H- benzotriazole-1-oxide, 4-
bromo-6-nitro-3H-benzotriazole-1- oxide, 6-bromo-4-nitro-3H-benzotriazole-1-oxide, 5-chloro-3H-
15 benzotriazole-1-oxide, 6-chloro-3H-benzotriazole-1-oxide, 4- chloro-6-nitro-3H-benzotriazole-1-
oxide, 4,6-dibromo-3H-benzotriazole-1-oxide, 4,6-dibromo-3-methyl-3H-benzotriazole- 1-oxide,
4,6-dichloro-3H-benzotriazole-1-oxide, 4,7-dichloro- 3H-benzotriazole-1-oxide, 5,6-dichloro-3H-
benzotriazole-1- oxide, 4,6-dichloro-3-methyl-3H-benzotriazole-1-oxide, 5,7- dichloro-6-nitro-3H-
benzotriazole-1-oxide, 3,6-dimethyl-6- nitro-3H-benzotriazole-1-oxide, 3,5-dimethyl-6-nitro-3H-
20 benzotriazole-1-oxide, 3-methyl-3H-benzotriazole-1-oxide, 5- methyl-3H-benzotriazole-1-oxide, 6-
methyl-3H-benzotriazole-1- oxide, 6-methyl-4-nitro-3H-benzotriazole-1-oxide, 7-methyl-6- nitro-
3H-benzotriazole-1-oxide, 5-chloro-6-nitro-3H- benzotriazole-1-oxide.

Further examples of compounds of formulas IV and V are 2H-benzotriazole-1-oxides, such as:

(2-(4-acetoxyphenyl)-2H-benzotriazole-1-oxide, 6- acetylamino-2-phenyl-2H-benzotriazole-1-oxide, 2-(4- ethylphenyl)-4,6-dinitro-2H-benzotriazole-1-oxide, 2-(3- aminophenyl)-2H-
5 benzotriazole-1-oxide, 2-(4-aminophenyl)-2H- benzotriazole-1-oxide, 6-amino-2-phenyl-2H-
benzotriazole-1- oxide, 5-bromo-4-chloro-6-nitro-2H-benzotriazole-1-oxide, 2- (4-bromophenyl)-
2H-benzotriazole-1-oxide, 5-bromo-2-phenyl- 2H-benzotriazole-1-oxide, 6-bromo-2-phenyl-2H-
benzotriazole- 1-oxide, 2-(4-bromophenyl)-4,6-dinitro-2H-benzotriazole-1- oxide, 2-(4-
bromophenyl)-6-nitro-2H-benzotriazole-1-oxide, 5- chloro-2-(2-chlorophenyl)-2H-benzotriazole-1-
10 oxide, 5-chloro- 2-(3-chlorophenyl)-2H-benzotriazole-1-oxide, 5-chloro-2-(2,4- dibromophenyl)-2H-
benzotriazole-1-oxide, 5-chloro-2-(2,5- dimethylphenyl)-2H-benzotriazole-1-oxide, 5-chloro-2-(4-
nitrophenyl)-2H-benzotriazole-1-oxide, 5-chloro-6-nitro-2H-benzotriazole-1-oxide, 2-[4-(4-chloro-3-
nitrophenylazo)-3- nitrophenyl]-4,6-dinitro-2H-benzotriazole-1-oxide, 2-(3-chloro-4-nitrophenyl)-
4,6-dinitro-2H-benzotriazole-1-oxide, 2-(4-chloro-3-nitrophenyl)-4,6-dinitro-2H-benzotriazole-1-
15 oxide, 4-chloro-6-nitro-2-p-tolyl-2H-benzotriazole-1-oxide, 5-chloro-6-nitro-2-p-tolyl-2H-
benzotriazole-1-oxide, 6- chloro-4-nitro-2-p-tolyl-2H-benzotriazole-1-oxide, 2-(2- chlorophenyl)-
2H-benzotriazole-1-oxide, 2-(3-chlorophenyl)- 2H-benzotriazole-1-oxide, 2-(4-chlorophenyl)-2H-
benzotriazole-1-oxide, 5-chloro-2-phenyl-2H-benzotriazole-1- oxide, 2-[4-(4-chlorophenylazo)-3-
nitrophenyl]-4,6-dinitro- 2H-benzotriazole-1-oxide, 2-(2-chlorophenyl)-4,6-dinitro-2H-
20 benzotriazole-1-oxide, 2-(3-chlorophenyl)-4,6-dinitro-2H- benzotriazole-1-oxide, 2-(4-
chlorophenyl)-4,6-dinitro-2H- benzotriazole-1-oxide, 2-{4-[N'-(3-chlorophenyl)hydrazino]-3-
nitrophenyl}-4,6-dinitro-2H-benzotriazole-1-oxide, 2-{4-[N'-(4-Chlorophenyl)hydrazino]-3-
nitrophenyl}-4,6-dinitro-2H- benzotriazole-1-oxide, 2-(2-chlorophenyl)-6-methyl-2H- benzotriazole-

1-oxide, 2-(3-chlorophenyl)-6-methyl-2H- benzotriazole-1-oxide, 2-(4-chlorophenyl)-6-methyl-2H- benzotriazole-1-oxide, 2-(3-chlorophenyl)-6-nitro-2H- benzotriazole-1-oxide, 2-(4-chlorophenyl)-6- nitro-2H- benzotriazole-1-oxide, 2-(4-chlorophenyl)-6-picrylazo-2H- benzotriazole-1-oxide, 5- chloro-2-(2,4,5-trimethylphenyl)-2H- benzotriazole-1-oxide, 4,5-dibromo-6-nitro-2-p-tolyl-2H-
5 benzotriazole-1-oxide, 4,5-dichloro-6-nitro-2-phenyl-2H- benzotriazole-1-oxide, 4,5-dichloro-6- nitro-2-p-tolyl-2H- benzotriazole-1-oxide, 4,7-dichloro-6-nitro-2-p-tolyl-2H- benzotriazole-1-oxide,
4,7-dimethyl-6-nitro-2-phenyl-2H- benzotriazole-1-oxide, 2-(2,4-dimethylphenyl)-4,6- dinitro-2H- benzotriazole-1-oxide, 2-(2,5-dimethylphenyl)-4,6- dinitro-2H-benzotriazole-1-oxide, 2-(2,4-
10 dimethylphenyl)-6- nitro-2H-benzotriazole-1-oxide, 2-(2,5-dimethylphenyl)-6-nitro-2H- benzotriazole-1-oxide, 4,6-dinitro-2-[3-nitro-4-(N'- phenylhydrazino)phenyl]-2H-benzotriazole-1- oxide, 4,6- dinitro-2-[4-nitro-4-(N'-phenylhydrazino)phenyl]-2H- benzotriazole-1-oxide, 4,6-dinitro-
15 2-phenyl-2H-benzotriazole- 1-oxide, 2-(2,4-dinitrophenyl)-4,6-dinitro-2H-benzotriazole- 1-oxide, 2- (2,4-dinitrophenyl)-6-nitro-2H-benzotriazole-1- oxide, 4,6-dinitro-2-o-tolyl-2H-benzotriazole-1- oxide, 4,6- dinitro-2-p-tolyl-2H-benzotriazole-1-oxide, 4,6-dinitro-2- (2,4,5-trimethylphenyl)-2H-
20 benzotriazole-1-oxide, 2-(4- methoxyphenyl)-2H-benzotriazole-1-oxide, 2-(4-methoxyphenyl)- 6- methyl-2H-benzotriazole-1-oxide, 5-methyl-6-nitro-2-m- toyl-2H-benzotriazole-1-oxide, 5- methyl- 6-nitro-2-m-tolyl- 2H-benzotriazole-1-oxide, 5-methyl-6-nitro-2-o-tolyl-2H- benzotriazole-1-oxide,
5-methyl-6-nitro-2-p-tolyl-2H- benzotriazole-1-oxide, 6-methyl-4-nitro-2-p-tolyl-2H- benzotriazole-
1-oxide, 6-methyl-2-phenyl-2H-benzotriazole-1- oxide, 4-methyl-2-m-tolyl-2H-benzotriazole-1-
25 oxide, 4-methyl- 2-o-tolyl-2H-benzotriazole-1-oxide, 4-methyl-2-p-tolyl-2H- benzotriazole-1-oxide,
6-methyl-2-m-tolyl-2H-benzotriazole-1- oxide, 6-methyl-2-o-tolyl-2H-benzotriazole-1-oxide, 6- methyl- 2-p-tolyl-2H-benzotriazole-1-oxide, 2-[1]naphthyl-4,6- dinitro-2H-benzotriazole-1-oxide, 2- [2]naphthyl-4,6-dinitro- 2H-benzotriazole-1-oxide, 2-[1]naphthyl-6-nitro-2H- benzotriazole-1-oxide,

2-[2]naphthyl-6-nitro-2H- benzotriazole-1-oxide, 2-(3-nitrophenyl)-2H-benzotriazole-1- oxide, 6-nitro-2-phenyl-2H-benzotriazole-1-oxide, 4-nitro-2- p-tolyl-2H-benzotriazole-1-oxide, 6-nitro-2-o-tolyl-2H- benzotriazole-1-oxide, 6-nitro-2-p-tolyl-2H-benzotriazole-1- oxide, 6-nitro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole-1- oxide, 2-phenyl-2H-benzotriazole-1-oxide, 2-o-tolyl-2H-
5 benzotriazole-1-oxide, 2-p-tolyl-2H-benzotriazole-1-oxide.

Also preferred are condensed N-heterocyclic compounds, such as triazolo and tetrazolo compounds, which can contain at least one N-hydroxy, oxime, N-oxy, N,N-dioxy function and along with N a further hetero atom such as O, S, Se, or Te.

Examples for this are:

[1,2,4]triazolo[4,3-a]pyridine,
[1,2,4]triazolo[1,5-a]pyridine,
[1,2,4]triazolo[4,3-a]quinoline,
[1,2,4]triazolo[4,3-b]isoquinoline,
[1,2,4]triazolo[3,4-a]isoquinoline,
[1,2,4]triazolo[1,5-b]isoquinoline,
[1,2,4]triazolo[5,1-a]isoquinoline,
[1,2,3]triazolo[1,5-a]pyridine,
[1,2,3]triazolo[4,5-b]pyridine,
[1,2,3]triazolo[4,5-c]pyridine,
20 [1,2,3]triazolo[1,5-a]quinoline,
[1,2,3]triazolo[5,1-a]isoquinoline,
[1,2,4]triazolo[4,3-b]pyridazine,
[1,2,4]triazolo[1,5-b]pyridazine,

5

[1,2,4]triazolo[4,5-d]pyridazine,

[1,2,4]triazolo[4,3-b]quinoline,

[1,2,4]triazolo[3,4-a]phthalazine,

[1,2,4]triazolo[4,3-a]pyrimidine,

[1,2,4]triazolo[4,3-c]pyrimidine,

[1,2,4]triazolo[1,5-a]pyrimidine,

[1,2,4]triazolo[1,5-c]pyrimidine,

[1,2,4]triazolo[4,3-c]quinazoline,

[1,2,4]triazolo[1,4-a]quinazoline,

[1,2,4]triazolo[1,5-c]quinazoline,

[1,2,4]triazolo[5,1-b]quinazoline,

[1,2,3]triazolo[1,5-a]pyrimidine,

[1,2,3]triazolo[1,5-c]pyrimidine,

[1,2,3]triazolo[4,5-d]pyrimidine,

[1,2,3]triazolo[1,5-a]quinazoline,

[1,2,3]triazolo[1,5-c]quinazoline,

[1,2,4]triazolo[4,3-a]pyrazine,

[1,2,4]triazolo[1,5-a]pyrazine,

[1,2,3]triazolo[4,5-b]pyrazine,

20

[1,2,4]triazolo[4,3-a]quinoxaline,

[1,2,3]triazolo[1,5-a]quinoxaline,

[1,2,4]triazolo[4,3-b][1,2,4]triazine,

[1,2,4]triazolo[3,4-c][1,2,4]triazine,

[1,2,4]triazolo[4,3-d][1,2,4]triazine,

[1,2,4]triazolo[3,4-f][1,2,4]triazine,

[1,2,4]triazolo[1,5-b][1,2,4]triazine,

[1,2,4]triazolo[5,1-c][1,2,4]triazine,

5 [1,2,4]triazolo[1,5-d][1,2,4]triazine,

[1,2,4]triazolo[4,3-a][1,3,5]triazine,

[1,2,4]triazolo[1,5-a][1,3,5]triazine,

tetrazolo[1,5-a]pyridine,

tetrazolo[1,5-b]isoquinoline,

10 tetrazolo[1,5-a]quinoline,

tetrazolo[5,1-a]isoquinoline,

tetrazolo[1,5-b]pyridazine,

tetrazolo[1,5-b]quinoline,

15 tetrazolo[5,1-a]phthalazine,

tetrazolo[1,5-a]pyrimidine,

tetrazolo[1,5-c]pyrimidine,

tetrazolo[1,5-a]quinazoline,

tetrazolo[1,5-c]quinazoline,

tetrazolo[1,5-a]pyrazine,

20 tetrazolo[1,5-a]quinoxaline,

tetrazolo[1,5-b][1,2,4]triazine,

tetrazolo[5,1-c][1,2,4]triazine,

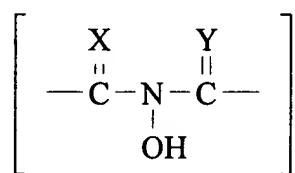
tetrazolo[1,5-d][1,2,4]triazine,

tetrazolo[5,1-f][1,2,4]triazine.

Other compounds that can be used according to the invention are: quinoline-N-oxide, isoquinoline-N-oxide, N-hydroxy-1,2,3,4-tetrahydroisoquinoline, β -(N-oxy-1,2,3,4-tetrahydroisoquinoline) propionic acid, 1,3-dihydroxy-2N-benzylimidobenzimidazoline.

5 Of the mediators disclosed in International Patent Disclosures WO 94/29425 and DE 4445088.5-43, 1-hydroxy-1H-benzotriazole (HBT) furnishes the best results as a bleach additive in multicomponent systems for use with detergents. However, HBT is available only at high prices and not in adequate amounts. Moreover, with the addition of laccase, for instance, it reacts to form 1H-benzotriazole (BT). This compound is relatively poorly degradable and in major 10 quantities could represent a major environmental burden. Moreover, its reaction speed is not very high and to a certain extent causes damage to the enzymes used. Additionally, HBT causes further colored decomposition products, which are undesirable.

Therefore those mediators that are very particularly preferred (which e.g. exhibit this undesired coloration only to a very limited extent) are those that are selected from the group of cyclical N-hydroxy compounds having at least one optionally substituted 5- or 6-member ring, containing the structure given in formula A:



Formula A

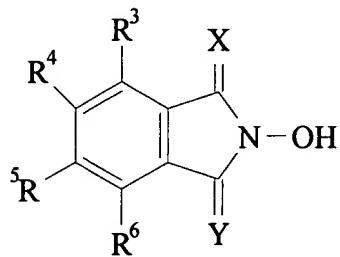
as well as their salts, ethers or ester, in which X and Y are the same or different and stand for O, S or

20 NR¹, in which

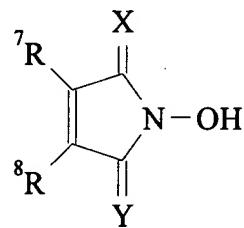
R¹ stands for hydrogen, hydroxyl, formyl, carbamoyl, or sulfono radical, or ester or salt of the sulfono radical, sulfamoyl, nitro, amino, phenyl, aryl C₁-C₅ alkyl, C₁-C₁₂ alkyl, C₁-C₅ alkoxy, C₁-C₁₀ carbonyl, carbonyl C₁-C₆ alkyl, phospho, phosphono or phosphonooxy radical, or ester or salt of the phosphonooxy radical; and carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or substituted once or multiple times with a radical R², and the aryl C₁-C₅ alkyl, C₁-C₁₂ alkyl, C₁-C₅ alkoxy, C₁-C₁₀ carbonyl, carbonyl C₁-C₆ alkyl radicals may be saturated or unsaturated, branched or unbranched, and substituted once or multiple times with a radical R² and R² is the same or different and stands for hydroxyl, formyl, or carboxyl radical, ester or salt of the carboxy radical, carbamoyl, sulfono ester or salt of the sulfono radical, sulfamoyl, nitro, amino, phenyl, C₁-C₅ alkyl, C₁-C₅ alkoxy radical.

The multicomponent systems of the invention contain mediators that are available on a large industrial scale and are less expensive than HBT. These mediators react under the influence of oxidation agents to form products without any problematic discoloration. These products in turn are completely degradable.

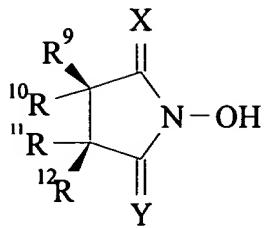
The multicomponent system according to the invention includes, as the mediator (component c), at least one compound of the general formula VI, VII, VIII or IX,



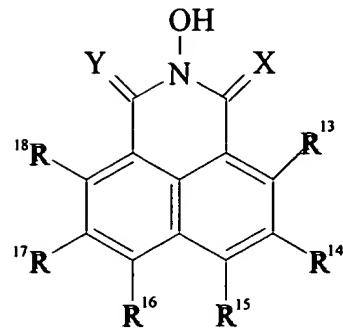
VI



VII



VIII

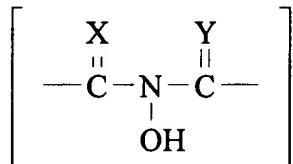


IX

in which X, Y have the meanings already given and the radicals R³ to R¹⁸ are the same or different

5 and stand for halogen radical, carboxy radical, salt or ester of a carboxy radical, or the meaning given for R¹; in which R⁹ and R¹⁰, or R¹¹ and R¹², must not at the same time stand for a hydroxyl or amino radical and optionally two at a time of the substituents R³ to R⁶, R⁷ to R⁸, R⁹ to R¹², R¹³ to R¹⁸ can be linked together into a ring -B-, in which -B- has one of the following meanings:

(-CH=CH)-_n, where n = 1 to 3, -CH=CH-CH=N-, or



Formula A

and in which optionally the radicals R⁹ to R¹² may also be linked to one another by one or two bridge elements -Q-, in which -Q- may be the same or different and can have the following meanings: -O-,

-S-, CH₂-, -CR¹⁹=CR²⁰-, in which R¹⁹ and R²⁰ are the same or different and have the same meaning as

15 R³.

Compounds that are especially preferred as mediators are those of the general formulas VI, VII, VIII or IX, in which X and Y stand for O or S.

Examples of such compounds are N-hydroxyphthalimide, and optionally substituted N-hydroxyphthalimide derivatives, N-hydroxymaleimide, optionally substituted N-hydroxymaleimide derivatives, N-hydroxynaphthalic acid imide, optionally substituted N-hydroxynaphthalic acid imide derivatives, N-hydroxysuccinimide, optionally substituted N-hydroxysuccinimide derivatives, 5 preferably those in which the radicals R⁹ to R¹² are polycyclically bonded.

N-Hydroxyphthalimide is especially preferred as the mediator (component c of the multicomponent system of the invention).

Compounds of formula VI that are especially suitable as mediators are for example:

N-hydroxyphthalimide, N-hydroxybenzene-1,2,4-tricarboxylic acid imide, N-N'-dihydroxypyromellitic acid diimide, N-N'-dihydroxybenzophenone-3,3',4,4'-tetracarboxylic acid diimide. 10

Examples of compounds of formula VII suitable as mediators are:

N-hydroxymaleimide, pyridine-2,3-dicarboxylic acid-N-hydroxyimide.

Examples of compounds of formula VIII suitable as mediators are:

N-hydroxysuccinimide, N-hydroxytartaric acid imide, N-hydroxy-5-norbornene-2,3-dicarboxylic acid imide, exo-N-hydroxy-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide, N-hydroxy-cis-cyclohexane-1,2-dicarboximide, N-hydroxy-cis-4-cyclohexane-1,2-dicarboxylic acid imide. 15

A compound of formula IX suitable as a mediator is for instance:

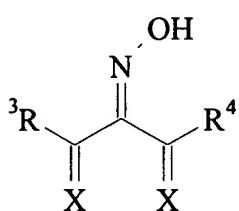
20 N-hydroxynaphthalic acid imide sodium salt.

A compound with a six-member ring containing the structure given in formula A suitable as a mediator is for instance:

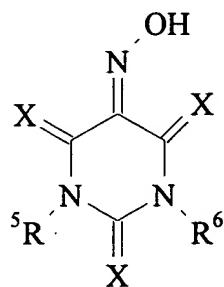
N-hydroxyglutarimide.

The compounds named as examples are also suitable as mediators in the form of their salts or esters.

Mediators that are very particularly preferred, also because of their low cost, good degradability, substantially lower "damage potential" to enzymes, and very fast reaction speed, are 5 those characterized in that they are selected from the group of oximes of the general formula X or XI



X



XI

and their salts, ethers or esters, in which X is the same or different and stands for O, S or NR¹, in which R¹ stands for hydrogen, hydroxyl, formyl, carbamoyl, or sulfono radical, or ester or salt of the sulfono radical, sulfamoyl, nitro, amino, phenyl, acryl C₁-C₅ alkyl, C₁-C₁₂ alkyl, C₁-C₅ alkoxy, C₁-C₁₀ carbonyl, carbonyl C₁-C₆ alkyl, phospho, phosphono or phosphonooxy radical, or ester or salt of the phosphonooxy radical; in which carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or substituted once or multiple times with a radical R², and the aryl C₁-C₅ alkyl, C₁-C₁₂

15 alkyl, C₁-C₅ alkoxy, C₁-C₁₀ carbonyl, carbonyl C₁-C₆ alkyl radicals may be saturated or unsaturated, branched or unbranched, and substituted once or multiple times with a radical R²; and

R² is the same or different and stands for hydroxy, formyl, or carboxy radical, ester or salt of the carboxy radical, carbamoyl, sulfono ester or salt of the sulfono radical, sulfamoyl, nitro, amino, phenyl, C₁-C₅ alkyl, C₁-C₅ alkoxy radical, and the radicals R³ and R⁴ are the same or different and

stand for halogen, carboxyl radical, ester or salt of the carboxyl radical, or have the meanings given for R¹, or are linked together into a ring (-CR⁷R⁸)_n, where n is equal to 2, 3 or 4, and

R⁵ and R⁶ have the meanings given for R₁, and

R⁷ and R⁸ are the same or different and stand for halogen, carboxyl radical, ester or salt of the

5 carboxyl radical, or have the meanings given for R¹.

Especially preferred as mediators in the multicomponent system of the invention are compounds with the general formula X, in which X stands for O or S and the other radicals have the meanings named above. One example of such a compound is 2-hydroxyiminomalonic acid dimethyl ester.

10 Also especially preferred as mediators are isonitro derivatives of cyclical ureides of general formula XI. Examples of such compounds are 1-methylvioluric acid, 1,3-dimethylvioluric acid, thiovioluric acid, and alloxane-4-5-dioxime.

Especially preferred as a mediator is alloxane-5-oxime hydrate (violuric acid) and/or its esters or salts.

15 Comediators

The components d) can contain for instance aliphatic ethers and/or aryl-substituted alcohols, such as:

2,3-dimethoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 2,4-dimethoxybenzyl alcohol,
2,6-dimethoxybenzyl alcohol, homovanillyl alcohol, ethylene glycol monophenyl ether, 2-
20 hydroxybenzyl alcohol, 4-hydroxybenzyl alcohol, 4-hydroxy-3-methoxybenzyl alcohol, 2-methoxybenzyl alcohol, 2,5-dimethoxybenzyl alcohol, 2,4-dimethoxybenzylamine, 2,4-dimethoxybenzylamine hydrochloride, veratryl alcohol, and coniferyl alcohol.

Olefins (alkenes) can also be considered, such as 2- allylphenol, 2-allyl-6-methylphenol, allylbenzene, 3,4- dimethoxypropylbenzene, p-methoxystyrene, 1-allylimidazol, 1-vinylimidizol, styrene, stilbene, allylphenyl ether, cinnamic acid benzyl ester, cinnamic acid methyl ester, 2,4,6-triallyloxy-1,3,5-triazine, 1,2,4-trivinylcyclohexane, 4-allyl-1,2-dimethoxybenzene, 4-tert-butylbenzoic acid vinyl ester, squalene, benzoin allyl ether, cyclohexene, dihydropyran, and N-benzylcinnamic acid anilide.

Phenol ethers are preferably used, such as 2,3- dimethoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 2,4- dimethoxybenzyl alcohol, 2,6-dimethoxybenzyl alcohol, homovanillyl alcohol, 4-hydroxybenzyl alcohol, 4-hydroxy-3- methoxybenzyl alcohol, 2-methoxybenzyl alcohol, 2,5- dimethoxybenzyl alcohol, 2,4-dimethoxybenzylamine, 2,4-dimethoxybenzylamine hydrochloride, veratryl alcohol, coniferyl alcohol, veratrol, and anisol.

Also preferred are carbonyl compounds, such as 4- aminobenzophenone, 4-acetyl biphenyl, benzophenone, benzil, benzophenone hydrazone, 3,4-dimethoxybenzaldehyde, 3,4-dimethoxybenzoic acid, 3,4-dimethoxybenzophenone, 4- dimethylaminobenzaldehyde, 4-acetyl biphenylhydrazone, benzophenone-4-carboxylic acid, benzoyl acetone, bis-(4,4-dimethylamino)benzophenone, benzoin, benzoin oxime, N- benzoyl-N-phenylhydroxyl-amine, 2-amino-5-chlorobenzophenone, 3-hydroxy-4-methoxybenzaldehyde, 4-methoxybenzaldehyde, anthraquinone-2-sulfonic acid, 4-methylaminobenzaldehyde, benzaldehyde, benzophenone-2-carboxylic acid, 3,3,’4,4’- benzophenonetetracarboxylic acid dianhydride, (S)-(-)-2-(N-benzylpropyl)-aminobenzophenone, benzylphenyl acetic acid anilide, N-benzylbenzalanilide, 4,4’-bis(dimethylamino)thiobenzophenone, 4,4- bis(diacetyl amino)benzophenone, 2-chlorobenzophenone, 4,4’- dihydroxybenzophenone, 2,4-dihydroxybenzophenone, 3,5- dimethoxy-4-hydroxybenzaldehyde hydrazine, 4- hydroxybenzophenone, 4-methoxybenzophenone, 3,4-

dihydroxybenzophenone, p-anisic acid, p-anisic aldehyde, 3,4- dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 3,5- dimethoxy-4-hydroxybenzaldehyde, 3,5-dimethoxy-4- hydroxybenzoic acid, 4-hydroxybenzaldehyde, salicylaldehyde, vanillin, and vannilic acid.

Component e)

5 By the addition of the compounds of the multicomponent system that are named under categories d) and e), a reaction mediation in cascade form, or recycling of the actual mediator compounds in situ, that is, during the reaction, ensues, and surprisingly leads to a substantial improvement in the bleaching reaction.

The multicomponent system contains as a free amine, in the case of the in situ generation or
10 reaction mediation in cascade form for hydroxybenzotriazol benzotriazole.

Further Components

In addition, the bleaching system may contain phenolic compounds and/or nonphenolic compounds with one or more benzene nuclei.

Along with the oxidation agents named above according to the invention, air, oxygen, H₂O₂, organic peroxides, sodium perborate, and/or sodium percarbonate are especially preferred.
15

Oxygen can also be generated in situ by means of H₂O₂+ catalase or similar systems or H₂O₂ from GOD + glucose or similar systems.

Also preferred is a multicomponent bleaching system containing cation-forming metal salts. As cations, Fe²⁺, Fe³⁺, Mn²⁺, Mn³⁺, Mn⁴⁺, Cu⁺, Cu²⁺, Ti³⁺, Cer⁴⁺, Mg²⁺, and Al³⁺ should be used.

20 The bleaching system can additionally contain polysaccharides and/or proteins. As polysaccharides, it is possible to use, among others, glucanes, mannanes, dextrans, levans, pectins, alginates, or vegetable rubbers, and/or its own polysaccharides formed by the fungi or produced in a mixed culture with yeasts. As proteins, gelatin or albumin among others can be used.

Other possible substances are simple sugar, oligomer sugar, amino acids, polyethylene glycols (PEG's), polyethylene oxides, polyethylene imines and polydimethyl siloxanes.

Use of the Multicomponent System

The multicomponent bleaching system of the invention can also be used in combination with
5 detergent additives known per se.

The bleaching system develops its effect in a pH range from 2 to 12, preferably from 4 to 10,
and at a temperature between 10°C and 60°C, and preferably between 20°C and 40°C.

The invention will be described in further detail below with reference to the examples:

Example 1

Influence of the laccase mediator system on standard cotton fabrics stained with coffee.

Example: In 100 ml of washing solution (in a 300 ml Erlenmeyer flask), one fabric cloth each (5 x 5 cm) is incubated at 40°C for 40 minutes while being shaken with reciprocation (120 rpm). Before the onset of incubation, the washing solution is subjected to a ten-minute temperature adaptation. The washing solution is made up with STW (standard tap water) at 14° dH ("dH" means German degree of hardness). As the enzyme dosage, 200 IU* of laccase from *Coriolus versicolor* per 100 ml is used, and as the mediator dosage, 200 mg of hydroxybenzotriazole per 100 ml is used.

After the "washwater" is poured off, the flask is filled with a cold, strong stream of water three times and poured off again.

20 Table 1 shows the results, in comparison with a commercial liquid detergent (without a bleaching system) and a solid detergent (with a bleaching system).

* 1 IU = conversion of 1 μ mol of Syringaldazine per min per ml enzyme

Table 1

	pH	Whiteness	Brightness
STW zero value	4.5	2.55	2.3
Solid detergent	10.1	8.9	6.15
STW + enzyme + mediator	4.5	5.0	5.8
Liquid detergent	4.5	3.85	3.75
Liquid detergent + enzyme + mediator	4.5	6.15	6.6

Example 2

Influence of the laccase mediator system on standard tea fabrics stained with coffee.

In 100 ml of washing solution (in a 300 ml Erlenmeyer flask), one fabric cloth each (5 x 5 cm) is incubated at 40°C for 40 minutes while being shaken with reciprocation (120 rpm).

Before the onset of incubation, the washing solution is subjected to a ten-minute temperature adaptation. The washing solution is made up with STW (standard tap water) at 14° dH. As the enzyme dosage, 200 IU of laccase from *Coriolus versicolor* per 100 ml is used, and as the mediator dosage, 200 mg of hydroxybenzotriazole per 100 ml is used.

After the "washwater" is poured off, the flask is filled with a cold, strong stream of water three times and poured off again.

Table 2 shows the results, in comparison with a commercial liquid detergent (without a bleaching system) and a solid detergent (with a bleaching system).

Table 2

	pH	Whiteness	Brightness
STW zero value	4.5	2.7	2.5
Solid detergent	10.1	8.95	8.6
STW + enzyme + mediator	4.5	4.2	4.7
Liquid detergent	4.5	4.7	4.7
Liquid detergent + enzyme + mediator	4.5	5.5	5.95

Example 3

An experiment was performed in accordance with Example 1.

Acetoxybenzotriazole was used as the mediator.

The results can be found in Table 3.

Table 3

	pH	Whiteness	Brightness
STW zero value	4.5	2.55	2.3
Solid detergent	10.1	8.9	6.15
STW + enzyme + mediator	4.5	5	6.1
Liquid detergent	4.5	3.85	3.75
Liquid detergent + enzyme + mediator	4.5	6.2	6.7